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OCTANE-CETANE RELATIONSHIP

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Sixty-six samples of gasolines, representing commercial, military, and federal specification materials, and experimental blends were evaluated for motor octane number, research octane number, and cetane number. Through statistical analyses of the data, linear relationships between octane numbers and cetane numbers of these fuels were developed.

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OCTANE-CETANE RELATIONSHIP

FINAL REPORT
AFLRL NO. 33

by

J. N. Bowden

A. A. Johnston

J. A. Russell

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prepared by

U. S. Army Fuels and Lubricants Research Laboratory

Southwest Research Institute

San Antonio, Texas

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I. INTRODUCTION

The relationship between octane numbers and cetane numbers for low-ignition quality fuels has become important for the Army in recent times because of the following factors:

- Diesel engines are the predominant power plants in combat and tactical vehicles. With the energy shortage, it becomes important to know the ignition quality of gasolines that could be used in these engines when diesel fuel is in short supply.

- The LD/LDS465 multifuel engines, utilized in a high density of Army vehicles, may be able to use some special and regular grade gasolines. Thus, a relationship between octane number and cetane number would help determine which gasolines could be used in these engines.

The object of this work, therefore, was to study the relationship of cetane and octane numbers by expanding on the work conducted at this laboratory in the middle 1960's.[1]* Special interest was focused on the possible effects of unleaded gasolines on the cetane-octane number relationships, since unleaded (or low lead) fuels will be the primary spark ignition engine fuel for the Army and government service vehicles in the near future.

II. APPROACH

A total of 66 gasoline samples, which included commercial gasolines of the premium, regular, low-lead, and unleaded varieties, full boiling range reference fuel blends both conventionally leaded and unleaded, and samples meeting Federal Specification VV-G-001690 (Army-MR) and VV-G-76b, were evaluated for cetane number, motor and research octane number, hydrocarbon type, and lead content. These data were subjected to a regression analysis computer program from which correlations for octane-cetane numbers were developed. The effects of other gasoline properties on these correlations were also investigated.

III. SUMMARY OF RESULTS

The data obtained on 66 samples of gasoline are shown in Table I. Equations for regression correlation lines derived for various expressions of octane number correlated with cetane numbers are shown in Table II. Figure 1 shows the correlation line for motor octane number and cetane number along with the actual determined values. The 95-percent confidence limits for cetane numbers of given motor octane numbers are indicated by the vertical lines at the extreme and middle of the correlation line. The data points shown in Figure 1 indicated an apparent effect of lead content on the cetane numbers of fuels with the same motor octane numbers. The unleaded gasolines had lower cetane numbers than the conventionally leaded fuels. To investigate this observation, two samples of full boiling range unleaded gasolines were treated at two levels with tetraethyl lead and evaluated for octane and cetane numbers. The data obtained are in Figure 2, indicating that the effect of lead content on the correlation is minimal if any. Since most unleaded gasolines contained more aromatic hydrocarbons than the leaded ones, it was theorized that the observed effect was due to hydrocarbon-type composition rather than lead content. Therefore, composition was investigated for possible effect on the correlation; since fuel sensitivity (RON − MON) reflects, to a large extent, fuel composition, two regression correlations were developed—one

*Superscript numbers in parentheses refer to the list of references at the end of this report.

for the fuels with high sensitivity (8 and above) and one for fuels with low sensitivity (below 7.9). These correlations, shown in Figure 3 and Table II, indicate that fuel sensitivity does have an effect on the MON – CN correlation. The linear equations for low- and high-sensitivity fuels have correlation coefficients that are closer to –1 than the overall MON – CN correlation.

The correlation equation for cetane number and research octane number, shown in Table II, was found to have the best correlation coefficient and the lowest standard error of estimate. The plot for this correlation, the 95-percent confidence limits, and the individually determined points are shown in Figure 4. Correlation equations for cetane numbers and research octane numbers of low and high sensitivity gasolines, shown in Table II, indicate a very slight effect of sensitivity which is not statistically significant within 95-percent confidence limits. The correlation coefficients for the low and high sensitivity fuels are virtually the same as that for the overall RON-CN correlation. Cetane numbers of iso-octane and n-heptane blends at several octane levels are shown in Figure 4 and the data are approaching the regression correlation line.

A regression correlation was also developed for cetane number and antiknock index, (R+M)/2, and is shown in Figure 5. As expected, the correlation coefficient for this expression lies between those for research and for motor numbers (Table II).

IV. DISCUSSION

The fuel data for 66 samples of commercial and reference gasolines listed in Table I were obtained suing the following methods: FIA (ASTM D 1319) for aromatics and olefins; atomic absorption spectrophotometry and lead content; ASTM D 2700 for motor octane number; and ASTM D2699 for research octane number. The cetane number determinations were made by ASTM Method D 613 employing the CFR engine with modifications to permit the measurement on low-cetane quality fuels (0 to 20 cetane numbers) as described by Urban and Gray.[1] The principal modifications were a thicker diaphragm (0.041 in.) than normal in the combustion pressure indicator and a spacer (3/8-in. thick) behind the compression plug to obtain higher compression ratios and to increase the injection pressure (2000 psi), thus reducing injection sticking. The ASTM delay meter and associated apparatus were replaced with the modified instrumentation normally used at AFLRL consisting of an injection nozzle pintle displacement transducer, a quartz crystal cylinder pressure transducer, and an oscilloscope. This instrumentation permits the determination of beginning of injection and start of rapid pressure rise.

The reproducibility of the ASTM Motor Octane Number Method states that the results for a given sample between two laboratories should not be considered suspect unless they differ by more than 1.2 at 80 MON, 1.0 at 90 MON, and 1.5 at 100 MON, based on 95-percent confidence level. The reproducibility of the ASTM Research Octane Number Method states that the results for a given sample between two laboratories should not be considered suspect unless they differ by more than 1.2 at 80 RON, 0.7 at 90 RON, 0.6 at 95 RON, and 0.7 at 100 RON, based on 95-percent confidence level. Data to define the repeatability (difference between two results on a single sample by the same operator), for both methods has not been developed by ASTM. The reproducibility of the ASTM Cetane Method states that a single rating can be expected to be within ±2 cetane numbers of the true value at the 95-percent confidence level for conventional diesel fuels. The repeatability of the cetane method is not defined. These statements indicate that the research method has slightly better precision than the motor method, and the cetane method has less precision than either octane method.

The cetane numbers of 39 of the gasoline samples reported herein were determined in duplicate and in a few cases in triplicate. The largest deviation between determinations on a single sample was 0.8 cetane number and the average deviation was ±0.1.

A. Primary Reference Fuels

The primary reference fuels used in the work performed during the 1960's were n-cetane and alpha-methyl naphthalene. The latter is no longer available as an ASTM reference grade fuel and has been replaced in the standard procedure with heptamethylnonane which was assigned a cetane number of 15. Since it was expected that many fuels used in this work would have cetane numbers below 15, a supply of 99-percent pure alpha-methyl naphthalene was obtained which is believed to be of higher purity than the old ASTM grade material.

To compare the two primary reference fuel series and the secondary reference fuel blends (U-9 and T-16 blends), a series of fuels were evaluated for compression ratios at 17-deg ignition delay and plotted against the cetane number to which each fuel was blended (Figure 6). In the range of 71 to 34 cetane numbers, the primary reference fuel blends (alpha-methyl naphthalene – n-cetane and heptamethylnonane – n-cetane) and the secondary reference blends gave virtually the same compression ratios. Below 34 cetane numbers, differences among the compression ratio obtained for the three reference fuels at given cetane numbers became apparent. The cetane for the U-9 secondary reference fuel is 20.7; therefore, compression ratios at lower cetane numbers could not be obtained for this series of blends. Heptamethylnonane has been assigned a cetane number of 15 in D 613; however, based on alpha-methyl naphthalene – n-cetane primary reference blends, the cetane number of heptamethylnonane was found to be 12.2. Because of the limitations of secondary reference fuels and the current ASTM-designated primary reference fuels, the alpha-methyl naphthalene – n-cetane reference fuel blends were used in this work. Had the heptamethylnonane – n-cetane reference fuels been used with some provision for extrapolation below 15 cetane number, it appears that the cetane numbers obtained for the various gasoline samples would have been approximately 2.8 numbers higher than those measured with the alpha-methyl naphthalene – n-cetane blends as primary reference fuels.

B. Properties of Gasolines

Approximately half of the gasolines evaluated in this program were either commercial fuels, and/or met the requirements of Federal Specifications VV-G-001690 (Army-MR) Gasoline, Automotive, Low Lead or Unleaded and VV-G-76b Gasoline, Automotive or Military Specification MIL-G-46015 (MR) Gasoline, Automotive, Combat, Referee Grade. The balance were full boiling range reference fuel blends which are used primarily for road octane evaluations in the Coordinating Research Council's cooperative road octane survey program. One sample was an unleaded gasoline to which an unknown quantity of kerosene or diesel fuel had been added.

C. Relationship to Earlier Work

Figure 7 shows plots of octane-cetane number relationships reported by B. Brewster and R.V. Kerley[2] and by C.M. Urban and J.T. Gray[1] compared to the motor octane-cetane number correlation obtained in this work. The differences observed can be attributed to the differences in fuels used to develop the correlations and to the precision of the octane

number and cetane number determinations. The correlation reported by Brewster and Kerley is based on fuels with cetane numbers covering virtually the entire cetane scale and included some alcohol-gasoline blends.

The Urban and Gray work utilized, for the most part, commercial premium and regular grade gasolines containing lead. The present work included unleaded and leaded reference fuels of low octane numbers in addition to commercial leaded premium and regular gasolines, but not higher boiling diesel fuels and gas oils as in the correlation reported by Brewster and Kerley. Using only the data for commercial premium and regular gasolines in the present work, a linear correlation approaching the Urban and Gray correlation was developed.

V. CONCLUSIONS

The results of this work led to the following conclusions:

- A satisfactory correlation of motor octane numbers with cetane numbers for gasolines in the 75- to 94-MON range was developed which has a standard error of estimate of ±1.71. The linear equation for this correlation differs from previous published ones due primarily to differences in the fuels used.

- The most significant result of this work was the observation that the research octane number-cetane number correlation with a standard error of estimate of ±1.09 appears to be much better than the motor octane number-cetane number correlation.

- A satisfactory correlation between antiknock index, (R+M)/2, and cetane number with a standard error of estimate of ±1.31 was also developed. This correlation would have a practical application inasmuch as service station gasoline pumps are currently being posted with antiknock index values as ruled by the Cost of Living Council.

LIST OF REFERENCES

(1) Urban, C.M. and Gray, J.T., "An Investigation of Methods for Determining Cetane Numbers of Low Ignition Quality Fuels," presented at SAE Mid-Year Meeting, Detroit, Michigan, May 1968.

(2) Brewster, B., and Kerley, R.V., "Automotive Fuels and Combustion Problems," presented at SAE National West Coast Meeting, Seattle, Washington, August 1963.

TABLES

TABLE 1. PROPERTIES OF GASOLINES

Code, AL- -G	Description (See Note)	Lead, g/gal	Aromatics, V%	Olefins, V%	RON	MON	R+M / 2	Sensitivity	Cetane Number
5066	FBRU	0.002	19	10	84.1	76.5	80.3	7.6	16.2
5066-2	FBRU	0.002	21	10	85.3	77.2	81.2	8.1	16.0
5066-3	FBRU	0.002	23	10	86.7	78.2	82.4	8.5	15.6
5066-4	FBRU	0.001	24	11	88.3	79.3	83.8	9.0	15.1
5066-5	FBRU	0.001	25	11	89.9	80.5	84.7	9.4	14.7
5067-6	FBRU	0.001	27	11	91.6	81.7	86.6	9.9	14.2
5067-7	FBRU	0.003	27	10	93.2	82.9	88.0	10.3	13.0
5067-8	FBRU	0.004	27	9	95.1	84.2	89.6	10.9	12.0
5067-9	FBRU	0.005	27	7	96.8	85.5	91.2	11.3	10.3
5067-10	FBRU	0.006	27	6	98.5	86.7	92.6	11.8	9.2
5068	FBRU	0.007	27	5	100.0	87.9	94.0	12.1	7.8
5224	(1)	0.01	---	---	84.5	76.4	80.4	8.1	18.1
4656	VV-G-001690	0.007	33	7	93.0	82.9	88.0	10.1	14.0
5242	Premium	0.006	33	0	100.1	92.6	96.4	7.5	8.2
5026	VV-G-001690	0.005	23	4	88.7	82.6	85.6	6.1	15.8
5208	VV-G-001690	0.002	30	32	95.5	84.4	90.0	11.1	12.1
5233	VV-G-001690	0.017	32	17	94.9	83.9	89.4	11.0	11.8
5244	VV-G-001690	0.001	25	14	91.4	83.6	87.5	7.8	14.6
5042	VV-G-001690	0.009	22	4	88.3	82.5	85.4	5.8	15.6
5050	VV-G-001690	0.004	21	3	88.9	82.8	85.8	6.1	15.7
4113	VV-G-001690	0.46	24	10	96.3	86.6	91.4	9.7	12.6
4659	VV-G-001690	0.36	31	6	94.7	84.2	89.4	10.5	13.5
5055	VV-G-001690	0.49	8	22	91.8	85.5	88.6	6.3	15.8
5056	VV-G-001690	0.45	32	9	95.5	87.1	91.3	8.4	13.2
5066/5237	FBRU/FBRL	0.625	17	8	83.7	77.9	80.8	5.8	17.6
5193	Low Lead	0.56	30	1	96.4	89.3	92.8	7.1	10.7
5200	Low Lead	0.32	33	2	92.8	85.5	89.2	7.3	12.8
5202	Low Lead	0.42	25	4	94.1	87.1	90.6	7.0	11.8
5207	Low Lead	0.49	24	5	95.4	88.5	92.0	6.9	11.8
5237	FBRL	1.25	14	7	83.0	79.2	81.1	3.8	18.3
5237-2	FBRL	1.32	16	7	84.9	80.4	82.6	4.5	17.7
5237-3	FBRL	1.39	18	7	86.6	81.7	85.6	4.9	17.0
5237-4	FBRL	1.46	20	7	88.4	82.8	87.0	5.6	15.9
5237-5	FBRL	1.53	22	7	90.1	83.8	88.2	6.3	15.3
5237-6	FBRL	1.60	24	7	91.7	84.8	89.6	6.9	14.5
5237-7	FBRL	1.67	26	7	93.3	85.9	89.6	7.4	13.5
5237 8	FBRL	1.74	28	7	94.8	86.8	90.8	8.0	12.6
5238	FBRL	1.81	30	8	96.1	87.8	92.0	8.3	11.3
5238-10	FBRL	1.75	29	6	97.5	88.8	93.2	8.7	10.1
5238-11	FBRL	1.69	29	4	98.9	89.9	94.4	9.0	8.5
5239	FBRL	1.63	28	2	100.4	91.1	95.8	9.3	8.0
4692	VV-G-76b	1.63	30	2	91.9	85.4	88.6	6.5	15.6
4693	VV-G-76b	1.56	27	1	93.4	86.1	89.8	7.3	15.5
4694	VV-G-76b	1.56	26	2	92.9	85.3	89.1	7.6	15.3
4695	VV-G-76b	1.44	28	2	93.9	86.5	90.2	7.4	14.9
5067/5238	FBRU/FBRL	0.90	28	9	93.8	84.8	89.3	9.0	12.4
5068/5239	FBRU/FBRL	0.82	28	4	100.2	89.5	94.8	10.7	6.9
5192	Regular	3.19	25	3	92.8	87.8	90.3	5.0	14.1
5195	Regular	1.19	22	1	92.7	87.7	90.2	5.0	14.3

TABLE I. PROPERTIES OF GASOLINES (Cont'd)

Code, AL- -G	Description (See Note)	Lead, g/gal	Aromatics, V%	Olefins, V%	RON	MON	R+M / 2	Sensitivity	Cetane Number
5197	Regular	2.25	24	1	93.2	87.3	90.2	5.9	14.4
5199	Regular	2.56	25	3	93.8	87.4	90.6	6.4	13.9
5203	Regular	2.63	18	10	95.0	87.9	91.4	7.1	13.6
5205	Regular	2.69	19	6	93.3	87.2	90.2	6.1	15.1
5194	Premium	3.38	22	5	100.0	93.1	96.6	6.9	8.3
5196	Premium	2.75	28	2	99.0	92.6	95.8	6.4	9.0
5198	Premium	1.88	28	2	99.4	92.8	96.1	6.6	8.8
5201	Premium	3.13	27	4	100.1	93.7	96.9	6.4	7.8
5204	Premium	2.69	23	6	99.6	92.9	96.2	5.2	7.9
5206	Premium	2.44	22	3	99.9	93.9	96.9	6.0	8.1
5066-A	FBRU	0.002	19	10	85.0	75.7	80.4	9.3	16.5
5066-B	0.5ml MM	0.34	19	10	88.7	79.0	83.8	9.7	15.7
5066-C	3.0ml MM	1.86	19	10	93.9	85.5	89.7	8.4	13.4
5067-B	0.5ml MM	0.35	19	10	94.7	85.1	89.9	9.6	12.4
5067-C	3.0ml MM	1.88	19	10	99.0	89.5	94.2	9.5	8.6
5069	MIL-G-46015	3.94	26	5	91.3	83.2	87.2	8.1	15.5
5252	VV-G-001690	0.02	32	3	92.3	83.1	87.7	9.2	13.4

Note: FBRU–Full boiling range unleaded reference fuel blends, 1973 series RMFD 263, 264, 265-73.
(1)–Unleaded gasoline contaminated with diesel fuel.
VV-G-001690–Fuels meeting Interim Federal Specification VV-G-001690 (Army-MR) Gasoline, Automotive, Low Lead or Unleaded.
Premium–Commercial premium grade gasoline.
Low-lead–Commercial low-lead grade gasoline.
FBRL–Full boiling range leaded reference fuel blends, 1973 series, RMFD 266, 267, 268-73.
Regular–Commercial regular grade gasoline.
VV-G-76b–Fuels meeting Federal Specification VV-G-76b, Gasoline, Automotive.
MIL-G-46015–Fuels meeting Military Specification MIL-G-46015, Gasoline, Automotive, Combat, Referee Grade, Grade I.
FBRU/FBRL–1 to 1 blends of full boiling range fuels, unleaded and leaded.
MM–Added TEL as Motor Mix.

TABLE II. REGRESSION CORRELATIONS

Octane Number	Equation for Regression Correlation Line	Correlation Coefficient	Standard Error of Estimate	95% Confidence Limits at the Mean Octane No.
MON	CN=60.96–0.56 (MON)	–0.820	±1.71	±3.44
MON_L	CN=67.86–0.63 (MON_L)	–0.903	±1.32	±2.73
MON_H	CN=64.21–0.61 (MON_H)	–0.893	±1.24	±2.58
RON	CN=68.54–0.59 (RON)	–0.930	±1.09	±2.20
RON_L	CN=68.51–0.59 (RON_L)	-0.920	±1.20	±2.48
RON_H	CN=67.49–0.59 (RON_H)	–0.940	±0.94	±1.96
AI	CN=66.88–0.50 (AI)	–0.897	±1.31	±2.65

Definitions:

CN–Cetane Number.
MON–Motor Octane Number.
MON_L–Motor Octane Number, Low Sensitivity Fuel.
MON_H–Motor Octane Number. High Sensitivity Fuel.
RON–Research Octane Number.
RON_L–Research Octane Number, Low Sensitivity Fuel.
RON_H–Research Octane Number, High Sensitivity Fuel.
AI–Antiknock Index = (RON+MON)/2.
Correlation Coefficient–Tendency toward linearity (divergence from zero toward +1 or –1 indicative of stronger direct or inverse linear relationship).
Standard Error of Estimate– Vertical scatter of CN about the regression line.
95-Percent Confidence Limits–Upper and lower boundaries for the regression line with 0.95 probability of occurrence.

ILLUSTRATIONS

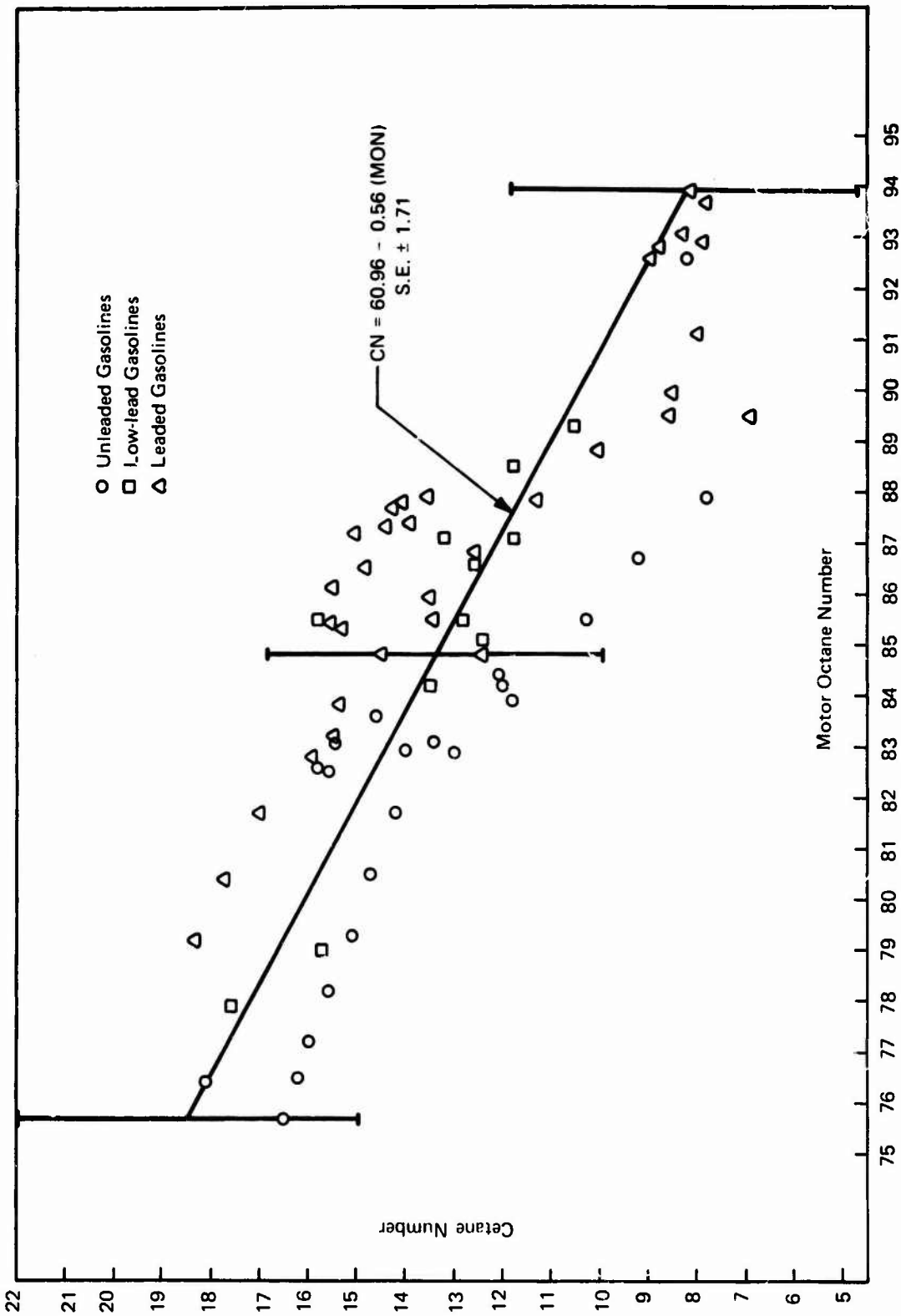

FIGURE 1. MOTOR OCTANE-CETANE NUMBER CORRELATION

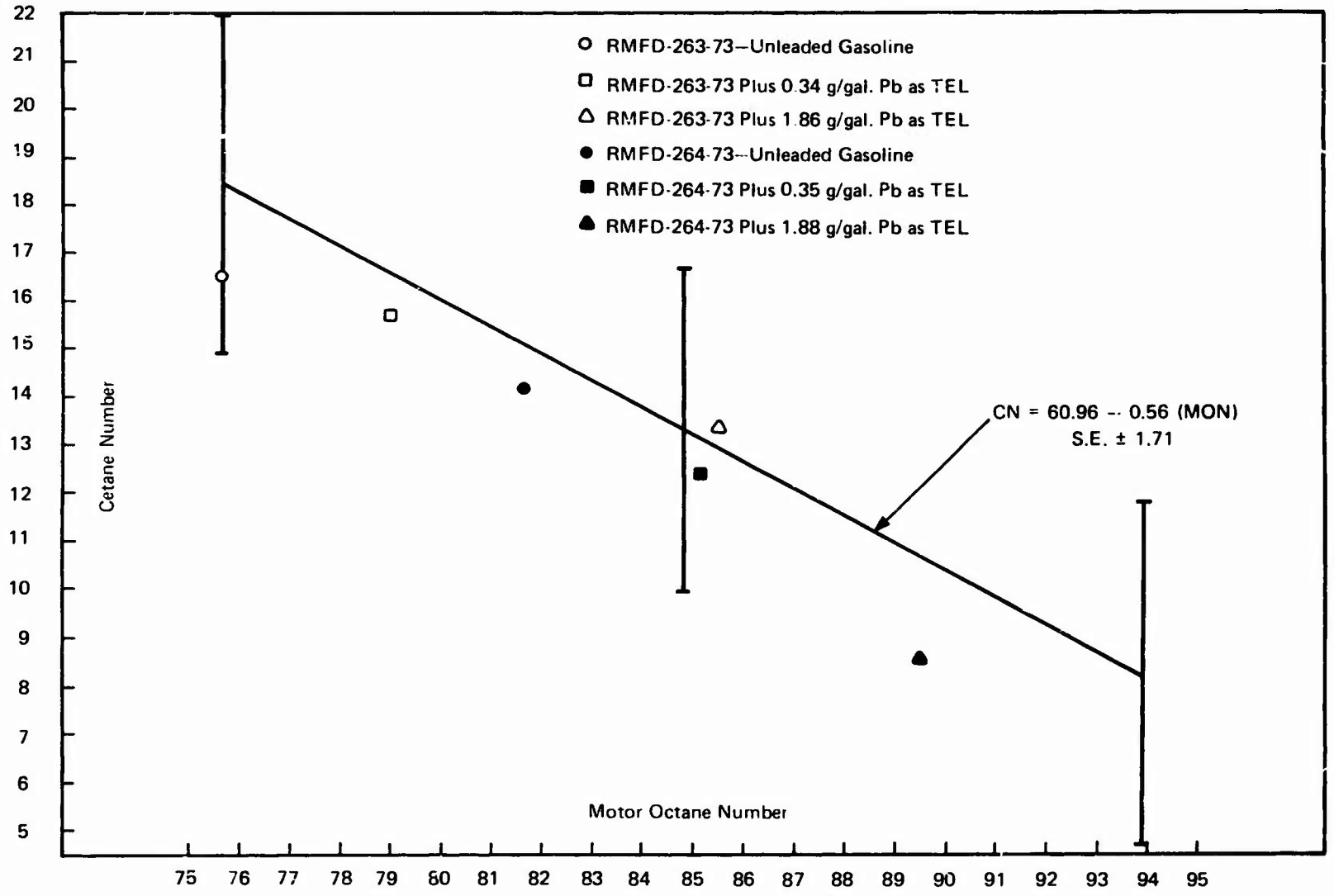

FIGURE 2. EFFECT OF LEAD ON MON-CN CORRELATION

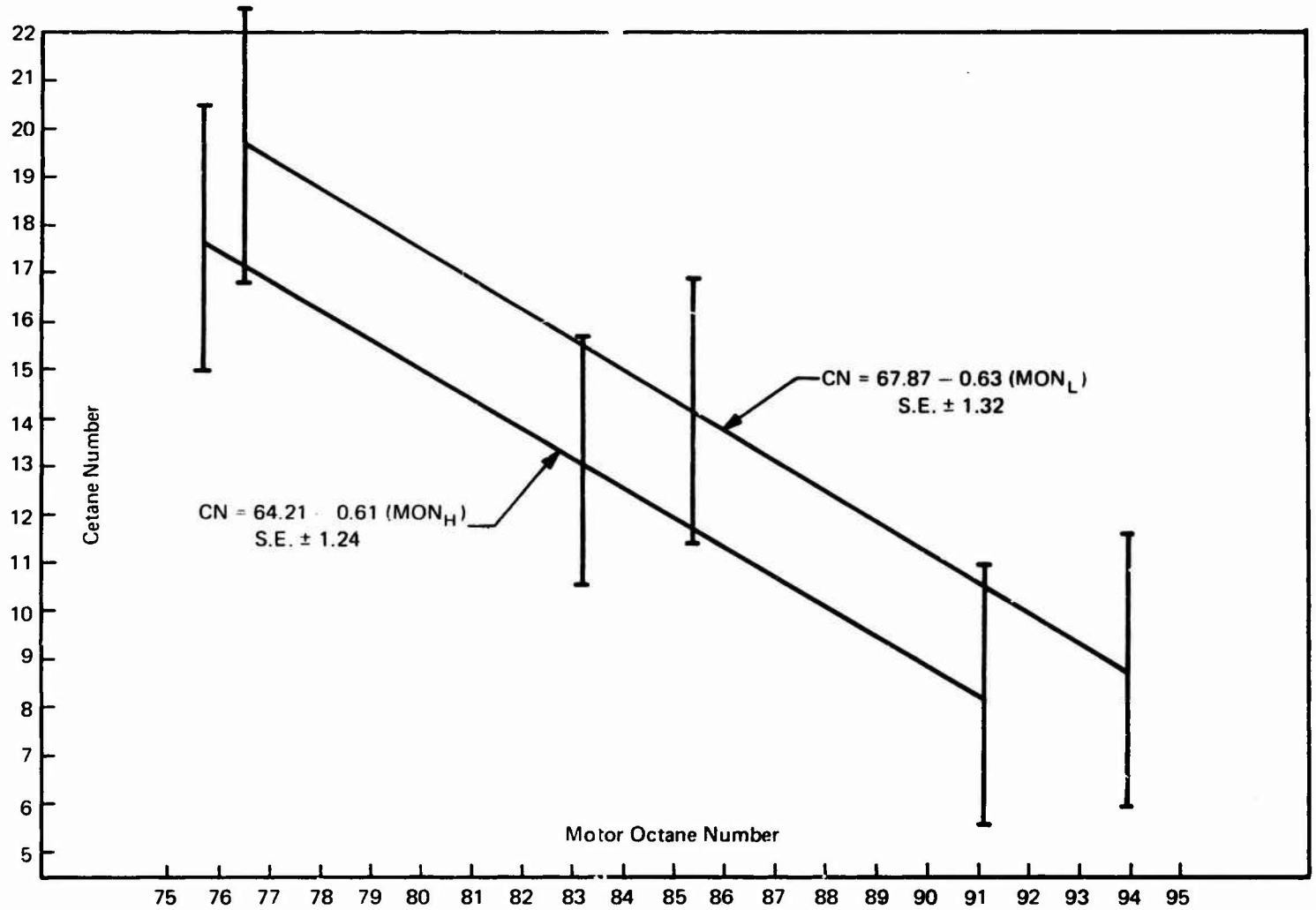

FIGURE 3. MON-CN CORRELATIONS FOR LOW AND HIGH SENSITIVITY FUELS

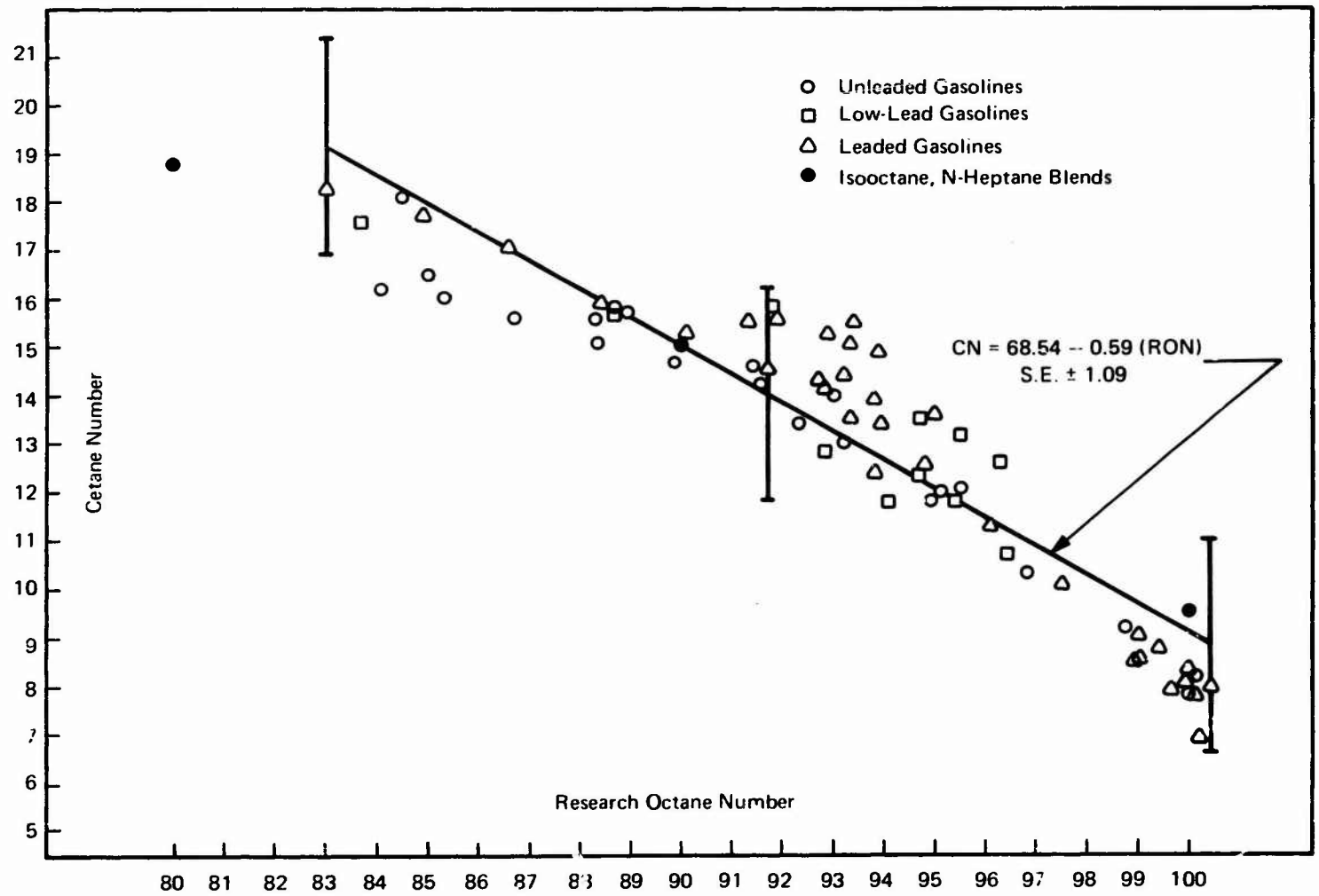

FIGURE 4. RESEARCH OCTANE-CETANE NUMBER CORRELATION

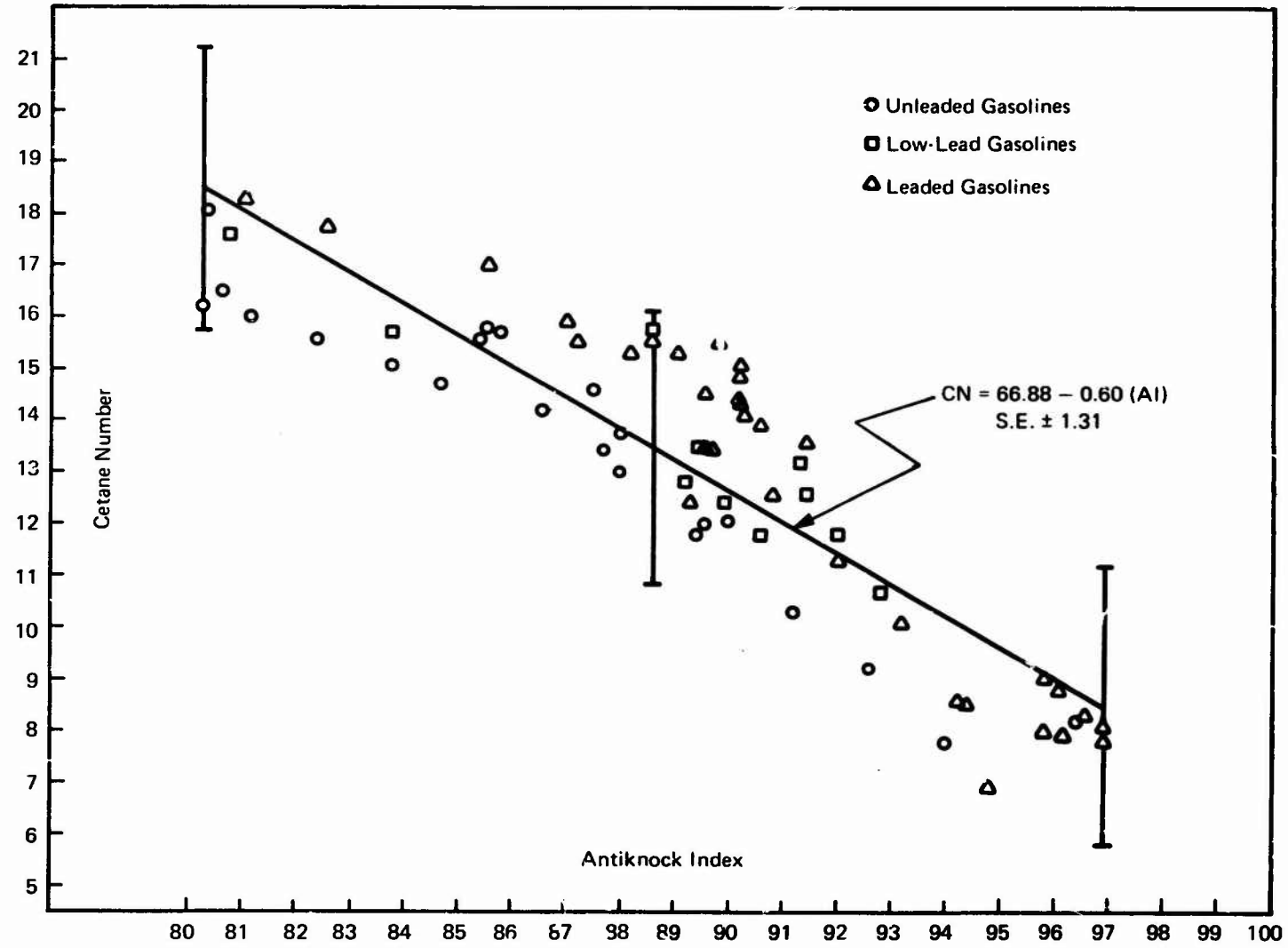

FIGURE 5. ANTIKNOCK INDEX-CETANE NUMBER CORRELATION

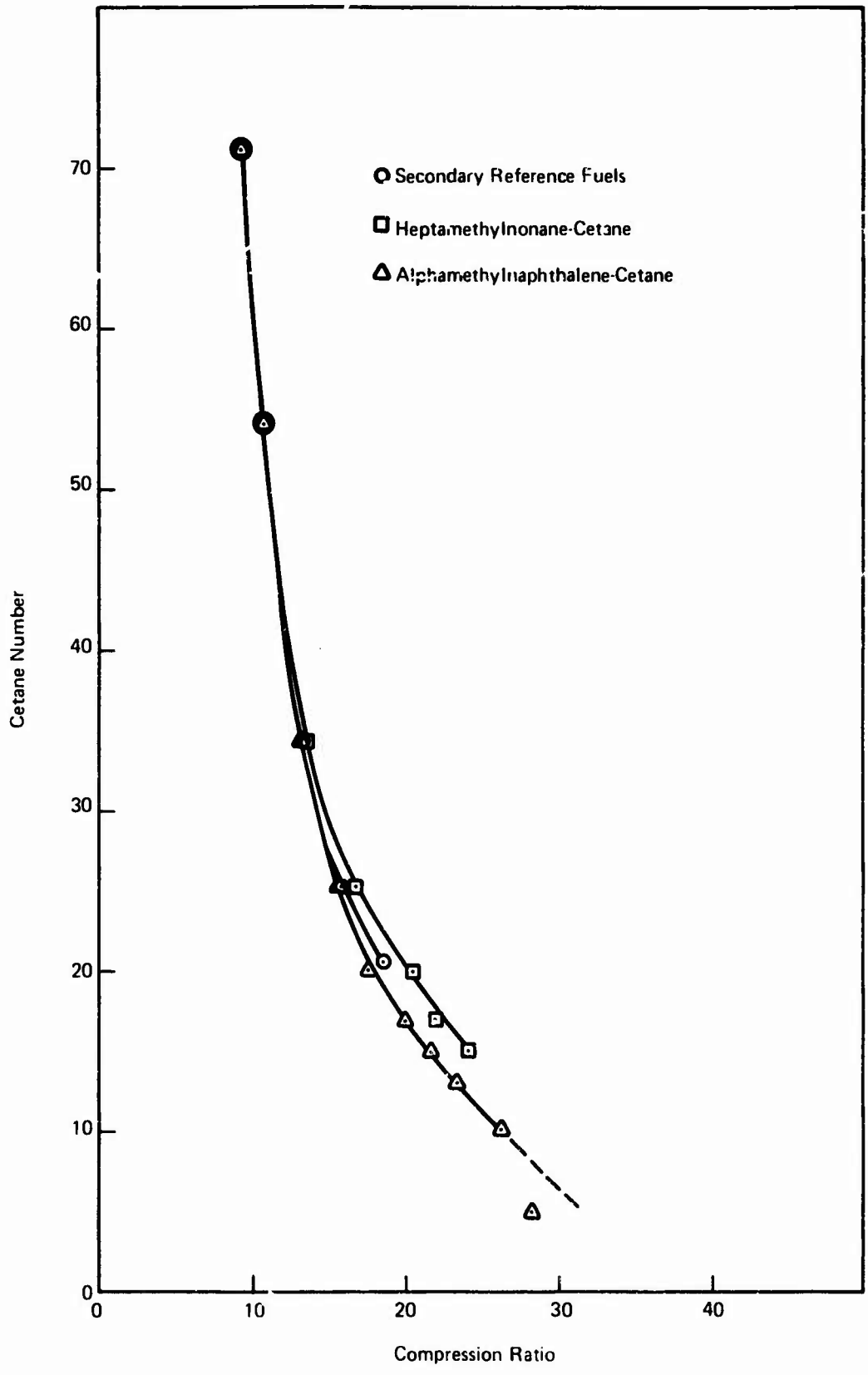

FIGURE 6. COMPRESSION RATIOS OF REFERENCE CETANE NUMBER BLENDS

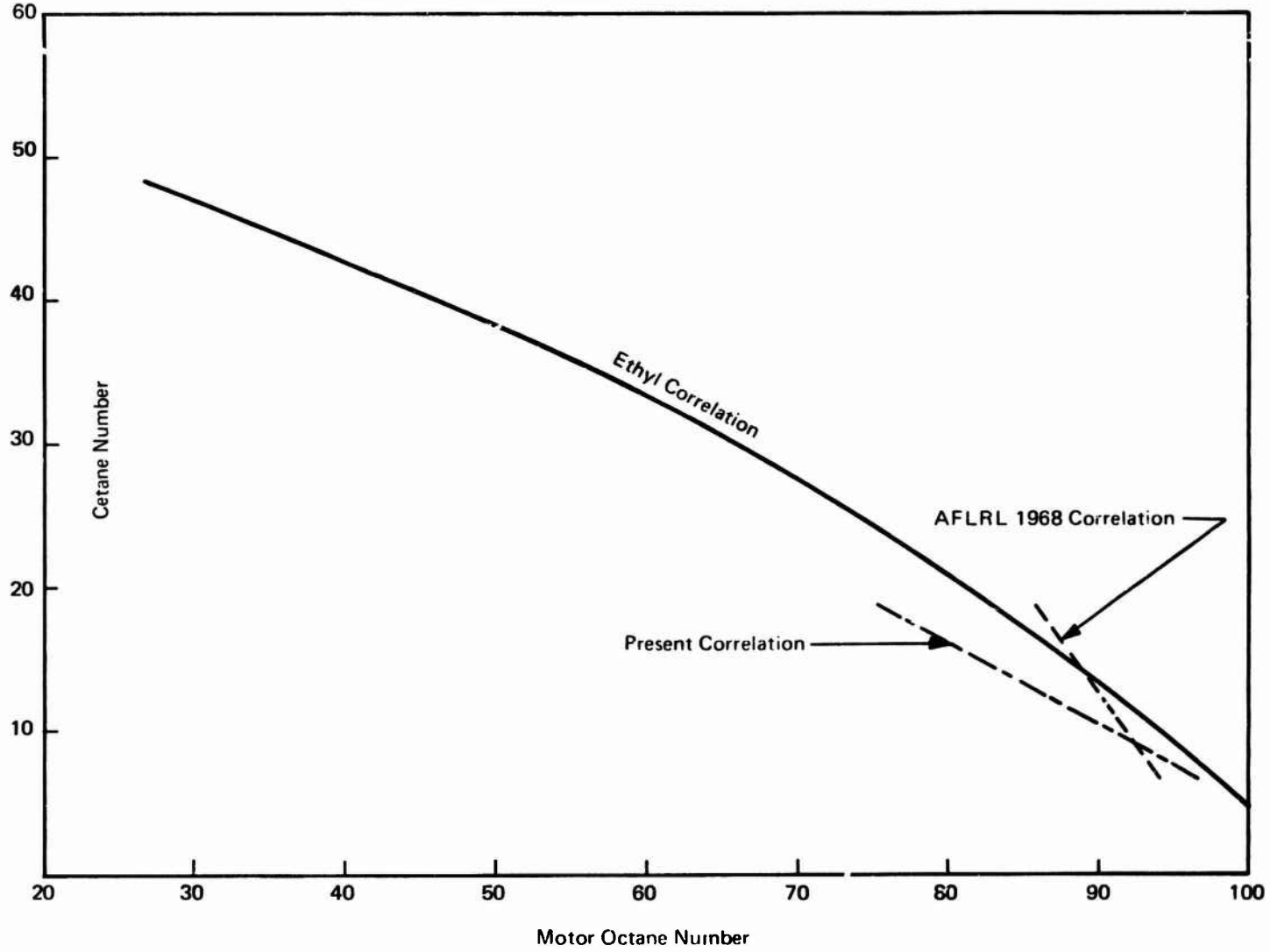

FIGURE 7. PRESENT WORK COMPARED TO PREVIOUS CORRELATIONS